Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pillar[5]arene Microcapsules Turn on Fluid Flow in Presence of Paraquat

Rohit Varshney,[a] Mujeeb Alam,[a] Chinmayee Agashe,[a] Roymon Joseph*[b] and Debabrata Patra*[a]

[a] Institute of Nano Science and Technology, Phase-10, Sector-64, Mohali, Punjab 160062.

[b] Department of Chemistry, University of Calicut, Calicut 673635, Kerala, India

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1. General Information

Water soluble cationic and anionic Pillar[5]arene derivatives were synthesized according to the literature and the molecular structure were shown in figure S1. All solvents and reagents were purchased from Sigma Aldrich and used as received without further modification. Millipore water (18.2 MΩ•cm at 25 °C) was used in all experiments. Malvern Zetasizer Nano ZSP (ZEN5600) was used for Zeta potential measurements. Transmission electron microscopy (TEM) was used to observed nanoaggregates with a JEOL JEM-2100 microscope operating at acceleration voltage 200KV. Microcapsules (MCs) were observed with an optical microscope (Olympus IX73 inverted microscope). The dried MCs and their morphology were observed with FESEM (Hitachi SU8010 series); the samples were coated with gold to render them conductive. The dynamic interfacial tension of the P$^{\oplus}$, P$^{\ominus}$ and P$^{\oplus}$-P$^{\ominus}$ nanoconjugates formed at the liquid-liquid interface was measured using the pendant drop method (Drop Shape Analyzer – DSA25 - KRÜSS GmbH). The absorbance for the host guest molecules and their complexes was measured by UV–vis spectrophotometer (UV-2600 ultraviolet-visible spectrophotometer SHIMADZU). Isothermal titration calorimetric measurements were performed on a Malvern MicroCal PEAQ-ITC. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C using 400 MHz and 500 MHz Bruker spectrometer with DMSO-d_6 and D_2O as solvent. Microparticles (polystyrene particles) tracking analysis of tracer particles was performed by Tracker software.

2. Experimental Section

Synthesis of $P^{\oplus}$ and $P^{\ominus}$: Experimental details for the synthesis of $P^{\oplus}$ and $P^{\ominus}$ is provided in supplementary information (see SI Figure S1-S7).

Synthesis of $P^{\oplus}$ $P^{\ominus}$ nanoaggregates: The nanoaggregates dispersion were prepared by mixing aqueous solutions of $P^{\oplus}$ (0.5mg/ml, pH = 3) and $P^{\ominus}$ (0.5mg/ml, pH = 8) at equal volume ratio (v/v). After mixing, the aqueous solution appeared to be white turbid dispersion and was drop casted on TEM grid for imaging.

MCs Preparation: In an Eppendorf tube, 800 µL of nanoaggregates were mixed with 40µL of oil (1,2,4-trichlorobenzene) and the mixture was shaken for 60 seconds using amalgamator. After shaking, the $P^{\oplus}$-$P^{\ominus}$ nanoagregates were assembled at the oil-water interface and appeared as white coloured MCs. These capsules were settled to the bottom of the tube and finally were washed several times with DI water to remove any free nanoaggregates.

Micropump Fabrication: To monitor the pumping ability of P[5]A MCs, a customized chamber [l= 1cm; w= 1cm, h= 1.8 mm] was made using FT-1201 mounting foam tape. All the MCs were carefully placed inside the chamber by using micropipette and the chamber was sealed by a PET sheet. It is important to create a leak proof chamber to avoid unwanted fluid flow and turbulence during measurement. To initiate the fluid pumping, an aqueous solution of PQ with suspended tracer particles (5 µm in diameter) was injected into the chamber and the fluid flow was observed by optical microscope.

Particle Tracking: The real time videos of particles motion was captured for further analysis. For measuring fluid velocity, 20 particles were tracked for 30s using Tracker, a motion analysis software.

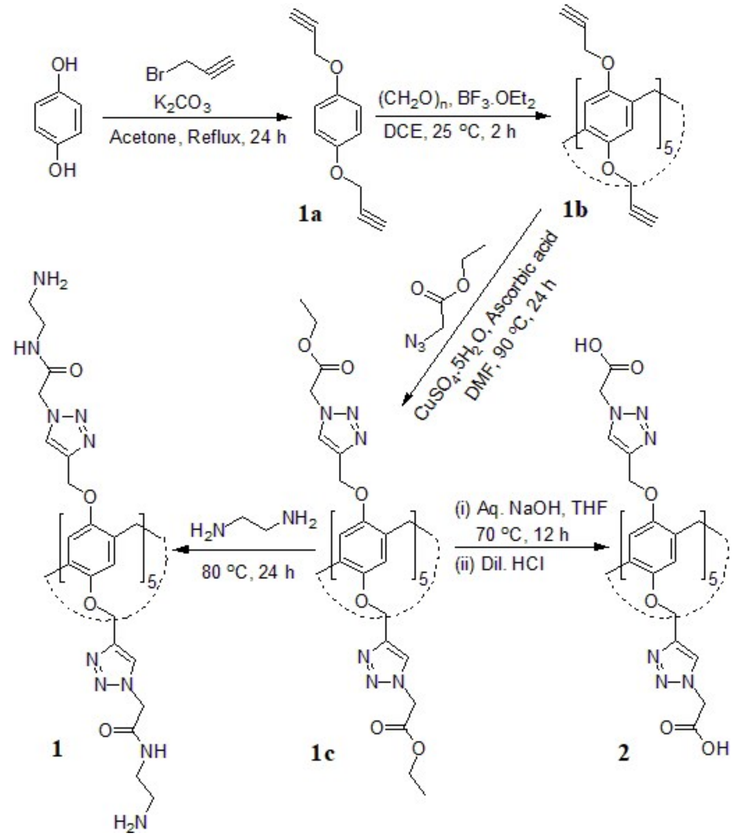


Figure S1. Experimental scheme for the synthesis of $P^{\oplus}$ (1), $P^{\ominus}$ (2) and its precursor (1c).

Synthesis of 1c.[1] A mixture of **1b**[2] (1.0 g, 1.2 mmol), ethyl azidoacetate[3] (2.3 g, 17.8 mmol), $CuSO_4.5H_2O$ (71 mg, 0.28 mmol) and ascorbic acid (0.37 g, 1.9 mmol) in DMF (40 mL) were kept at 90 °C for 24 h. The reaction mixture was cooled to 25 °C and solvents were evaporated. The solid was dissolved in dichloromethane (100 mL), washed with water (2 × 50 mL), brine (2 × 50 mL) and dried with Na_2SO_4. The solvent was evaporated and the product was purified by chromatography (silica gel; dichloromethane/methanol) to afford **1c** as white solid (1.6 g, 59%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.33 (s, Ar*H*, 10H), 6.95 (s, Ar*H*, 10H), 5.36 (s, OC*H*$_2$, 20H), 5.06 & 4.75 (br, NC*H*$_2$, 20H), 4.15-4.04 (m, OC*H*$_2$, 20H), 3.67 (s, ArC*H*$_2$Ar, 10H), 1.17 (t, *J* = 6.90 Hz, C*H*$_3$, 30H) ppm. ^{13}C NMR (100 MHz): δ 167.1, 148.8, 143.4, 128.1, 125.5, 114.3, 61.47 (Ar*C* × 2), 50.3, 28.7, 13.8 ppm. Anal. Calcd for $C_{110}H_{130}N_{30}O_{30}.8.65H_2O$: C, 52.67; H, 5.92; N, 16.75. Found C, 52.00; H, 5.26; N, 17.44.

Synthesis of 1.[1] A mixture of **1c** (1.0 g, 0.43 mmol) and ethylene diamine (15 mL, 225 mmol) were kept at 80 °C for 24 h. The reaction mixture was cooled to 25 °C and the product was precipitated by the addition of diethyl ether (50 mL). The precipitate was filtered, and purified from methanol/diethylether to afford **1** (0.95 g, 92%) as light brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.29 (br, N*H*, 10H), 8.24 (s, Ar*H*, 10H), 6.95 (s, Ar*H*, 10H), 5.07-4.98 (m, CH_2, 30H), 4.70 (d, *J* = 10.7 Hz, CH_2), 3.65 (s, ArCH_2Ar, 10H), 3.07 (br, CH_2, 20H), 2.58 (br, CH_2, 20H) ppm. ^{13}C NMR (100 MHz): δ 165.6, 148.8, 142.9, 128.0, 125.7, 114.2, 61.2, 51.5, 42.6, 41.0, 28.7 ppm. MALDI-TOF calcd for $C_{105}H_{140}N_{50}O_{20}$ ($[M]^+$) 2422.55, found 2422.27.

Synthesis of 2. A solution of **1c** (1.0 g, 0.43 mmol) in tetrahydrofuran (20 mL) and 20% aqueous sodium hydroxide (25 mL) was kept at 70 °C for 12 h. Then the reaction mixture was evaporated under vacuum, diluted with water (20 mL) and acidified with dilute HCl solution. The resulting precipitate was filtered, washed with water, and dried to afford **2** (0.85 g, 97 %) as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.26 (s, Ar*H*, 10H), 6.99 (s, Ar*H*, 10H), 5.23 (s, *CH_2COOH*, 20H), 5.09 (d, *OCH_2*, *J* = 11 Hz, 10H), 4.78 (d, *OCH_2*, *J* = 11 Hz, 10H), 3.67 (s, *$ArCH_2Ar$*, 10H) ppm. ^{13}C NMR (100 MHz): δ 168.7, 148.9, 143.3, 128.3, 125.5, 114.5, 61.6, 50.6, 28.8 ppm. Anal. Calcd for $C_{85}H_{80}N_{30}O_{30}.11.56H_2O$: C, 46.16; H, 4.71; N, 19.00. Found C, 45.72; H, 4.27; N, 18.73.

3. NMR Characterization : ^{1}H and ^{13}C NMR of 1, 2, and its precursors

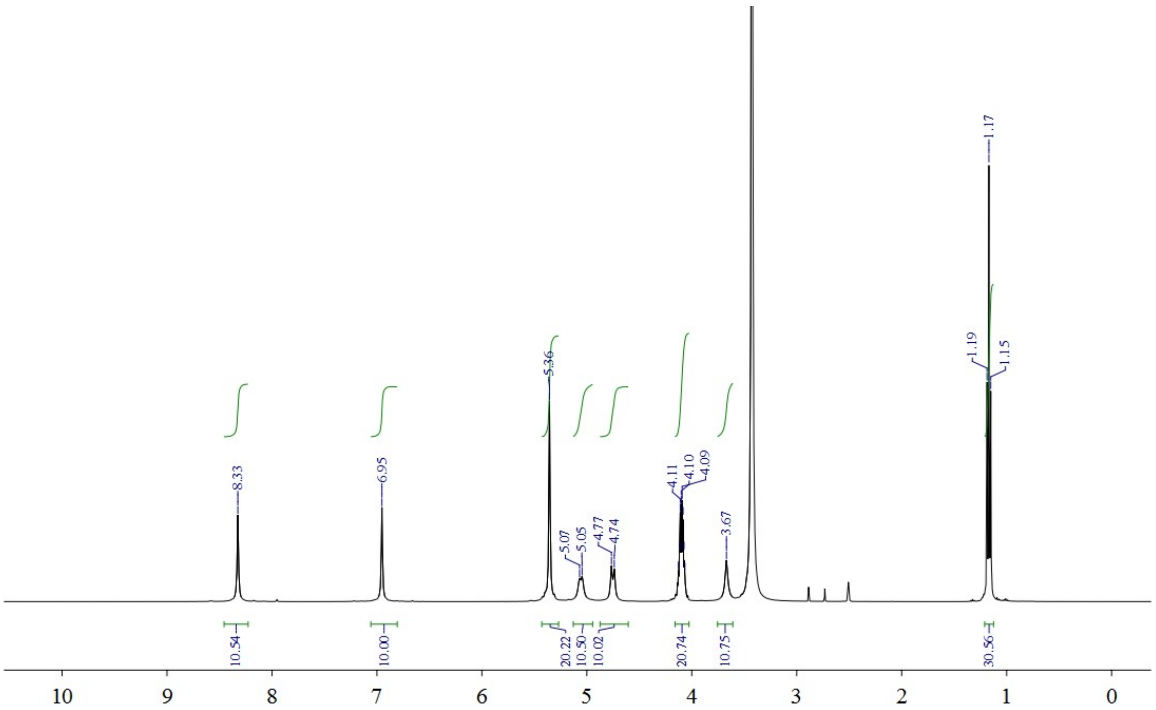


Figure S2. ^{1}H NMR spectrum of **1c** in DMSO-d_6 (400 MHz).

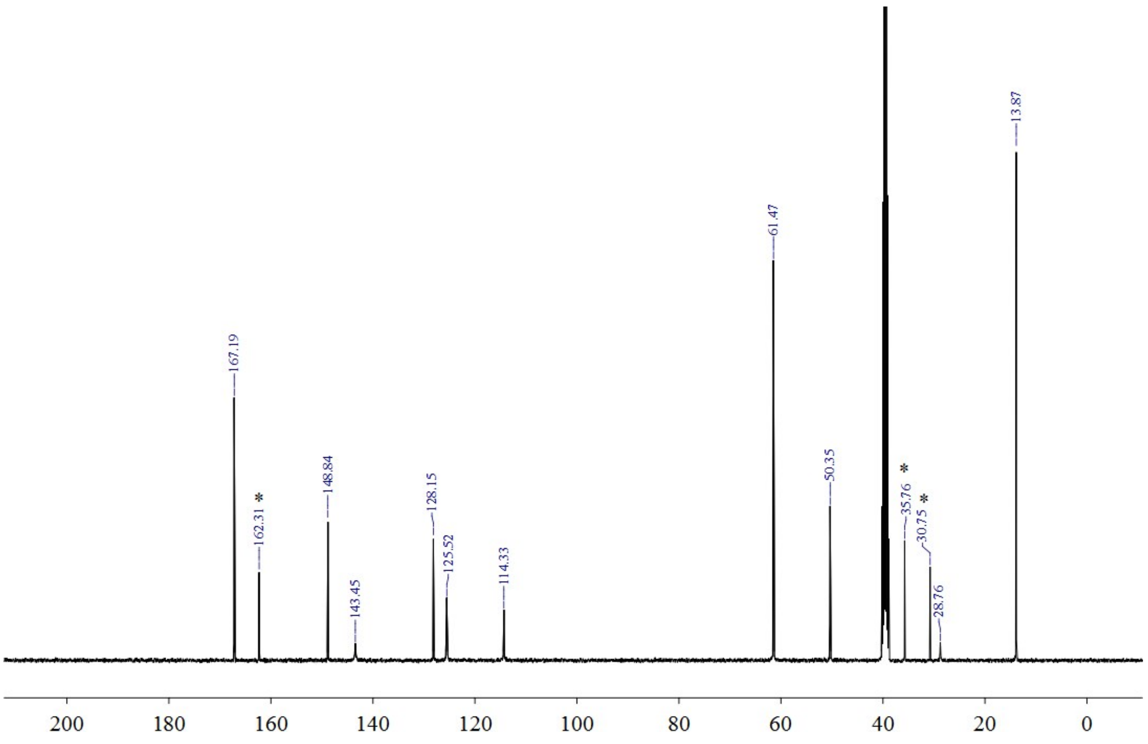


Figure S3. ^{13}C NMR spectrum of **1c** in DMSO-d_6 (100 MHz).

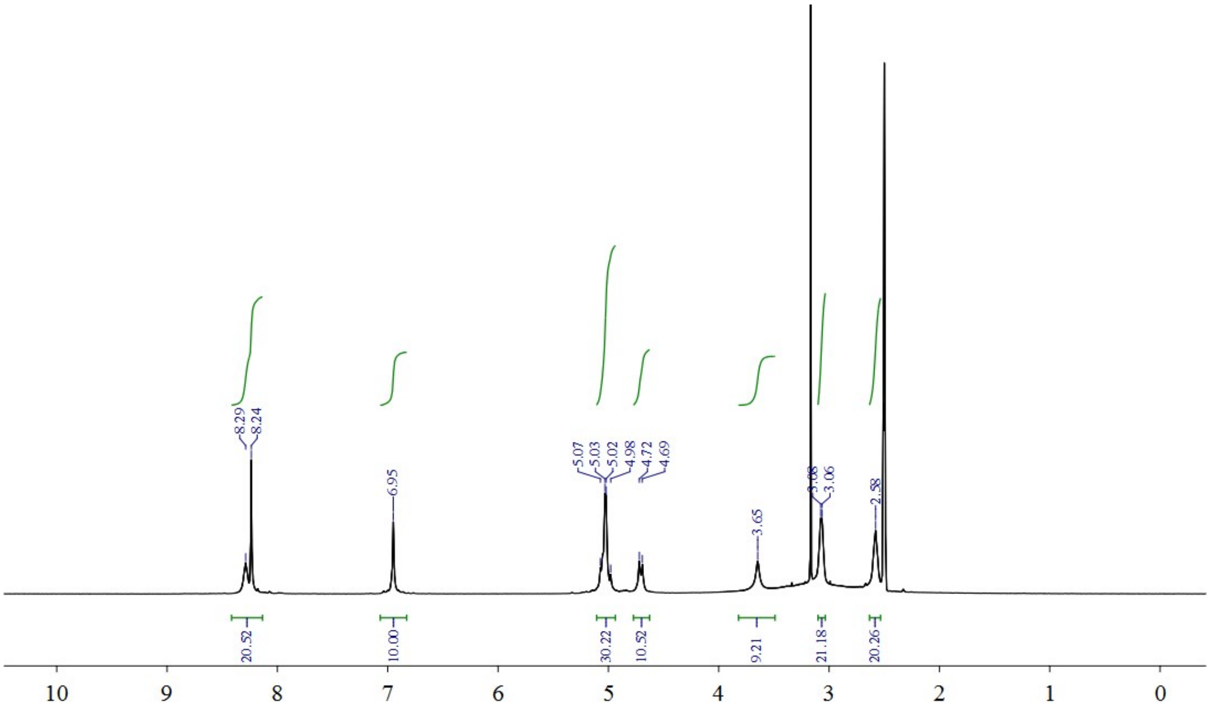


Figure S4. ^{1}H NMR spectrum of **1** in DMSO-d_6 (400 MHz).

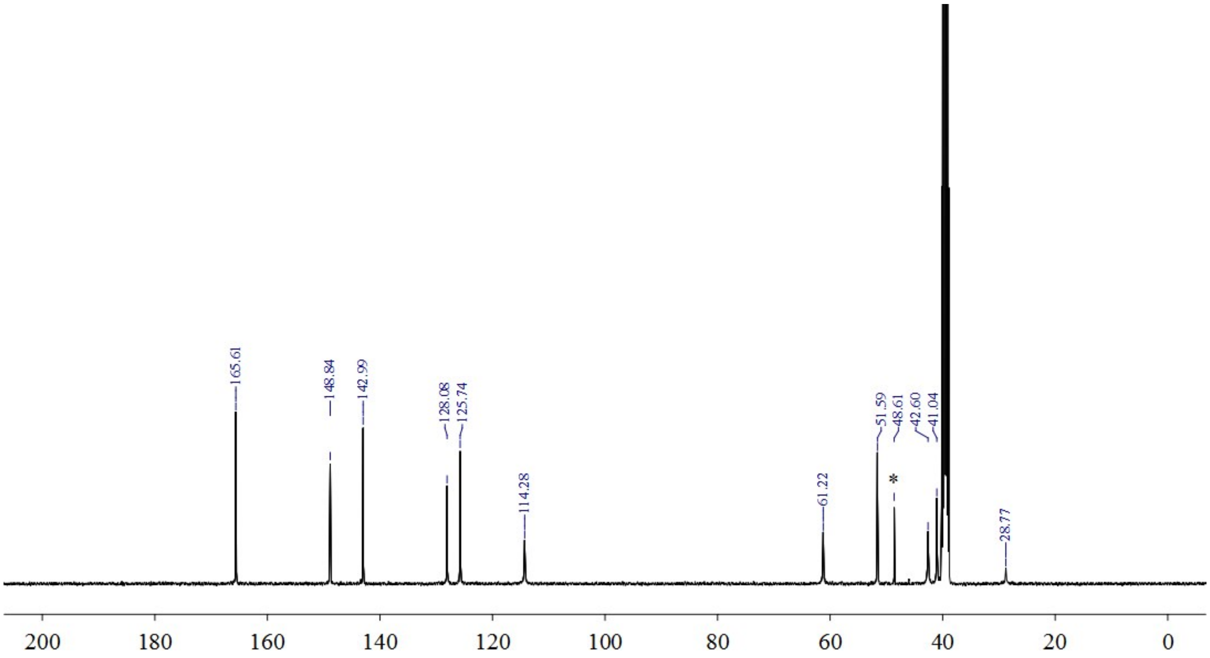


Figure S5. ^{13}C NMR spectrum of **1** in DMSO-d_6 (100 MHz). (*denotes methanol)

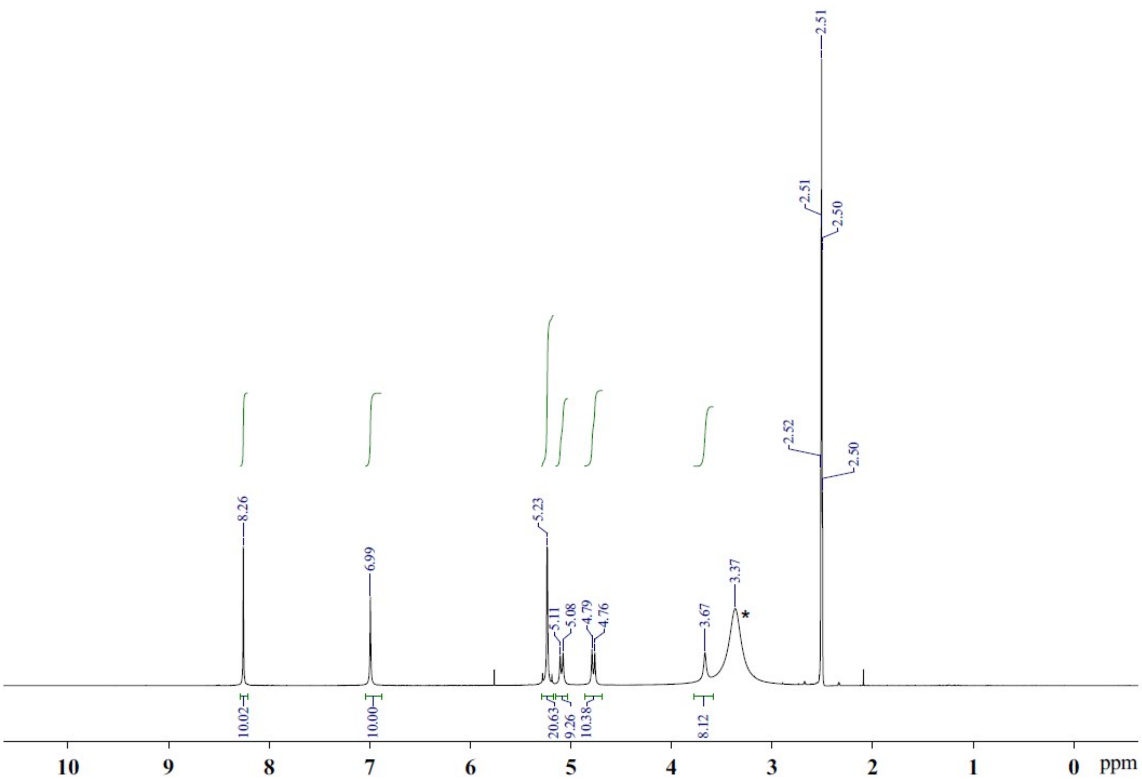


Figure S6. ^1H NMR spectrum of **2** in DMSO-d_6 (400 MHz). * denotes H_2O.

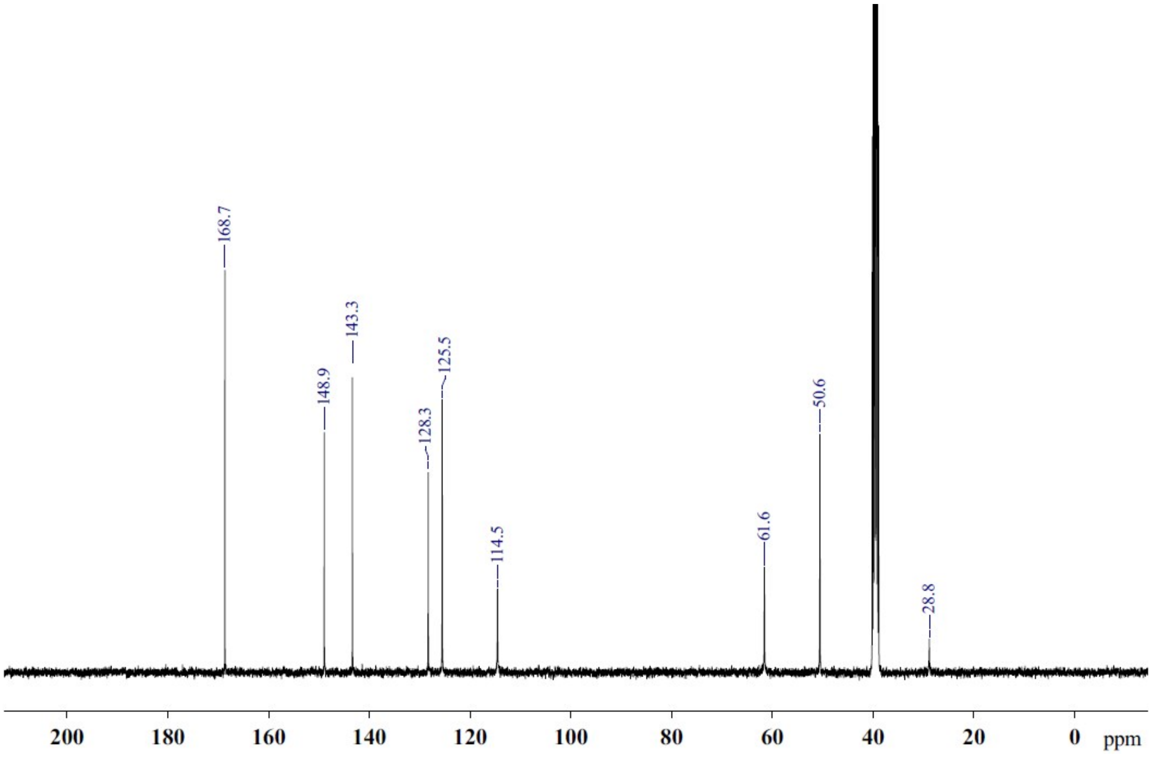
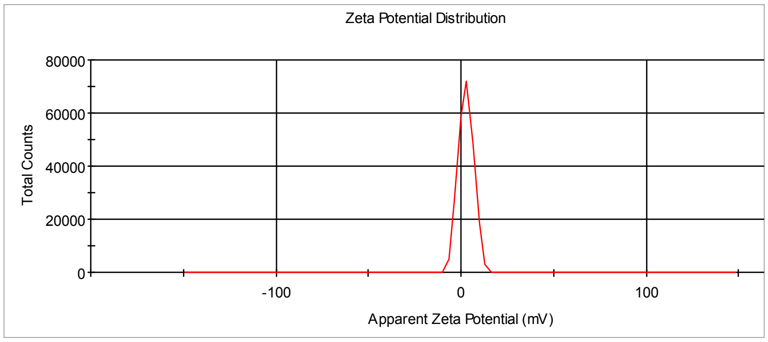


Figure S7. ^{13}C NMR spectrum of **2** in DMSO-d_6 (100 MHz).

4. Zeta Potential Measurements



P ⊕ : + 30.4 ± 0.80

P ⊖ : - 29.3 ± 2.91

P ⊕ - P ⊖ Nanoaggregates: +2.97 ±0.38

Figure S8. Zeta potential plot for P ⊕ P ⊖ nanocomplexes prepared with a nearly neutral surface charge (+2.97 ± 0.38 mV).

5. UV-Vis Absorption Spectra of Dried Nanoaggregates and pH Stability of the Aggregates.

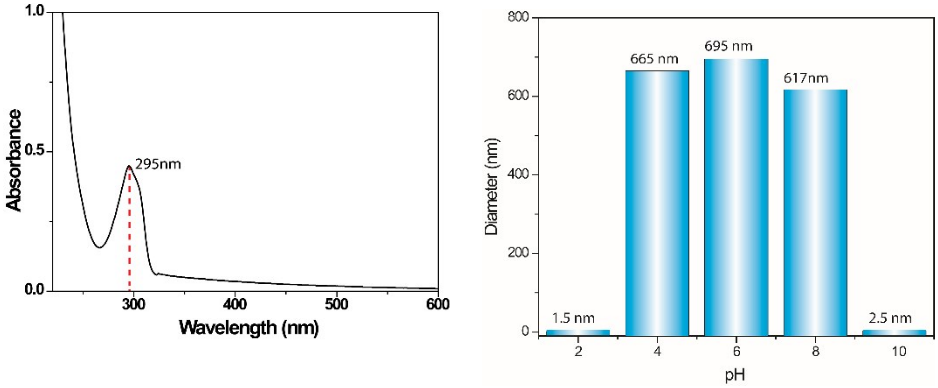


Figure S9. UV-Vis. absorption spectra of dried pillar[5]arene nanoaggregates and stability of the nanoaggregates at different pH

6. Size Distribution Analysis

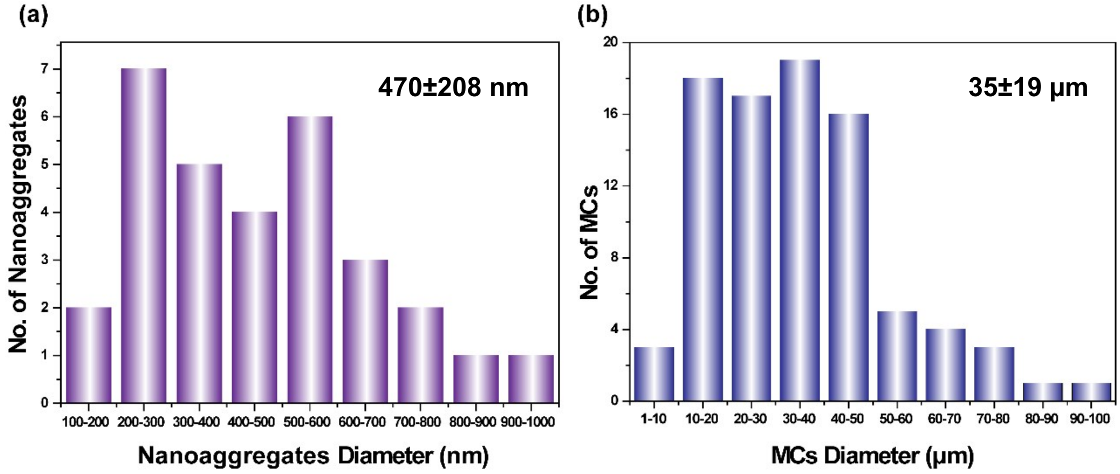


Figure S10. (a) P ⊕ - P ⊖ nanoaggregates size distribution plot; Mean diameter 470±208 nm. (b) Droplet size distribution of P ⊕ P ⊖ nanoaggregates stabilized MCs, showing polydispersity in sizes, mean diameter 35±19 µm.

7. Digital Images of $P^{\oplus}$, $P^{\ominus}$, $P^{\oplus}P^{\ominus}$ Nanoaggregates Stabilized MCs after Emulsification

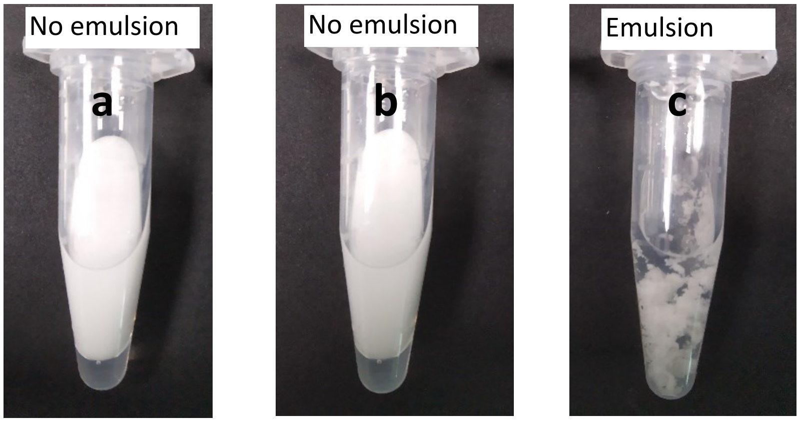


Figure S11. *An attempt was made to synthesize emulsions using (a)* $P^{\oplus}$ and (b) $P^{\ominus}$. No emulsions were formed, only phase separation occurred. (c) pillar[5]arene nanoaggregates stabilized MCs where MCs were settled down at the bottom after emulsification .

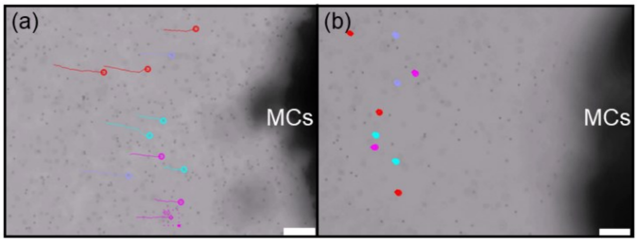


Figure S12. Tracer particles trajectories (a) Directional motion in presence of PQ (b) Random Brownian motion in absence of PQ. Scale bar is 100µm.

8. Tracer Particles Trajectories

9. Spatial and Spacer Height Profile for Fluid Pumping Mechanism

10. ITC Titration of Anionic Pillar[5]arene with Paraquat

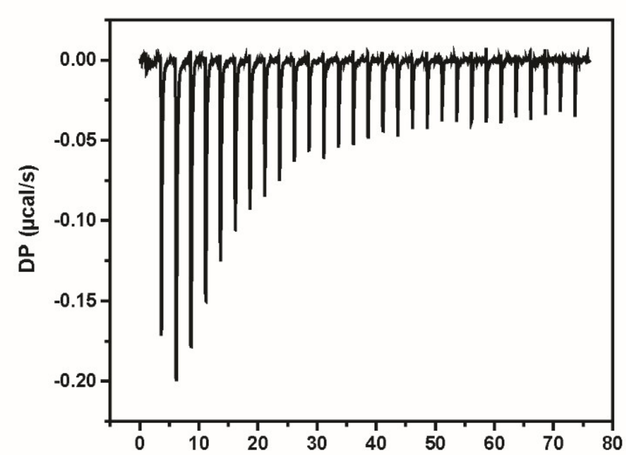
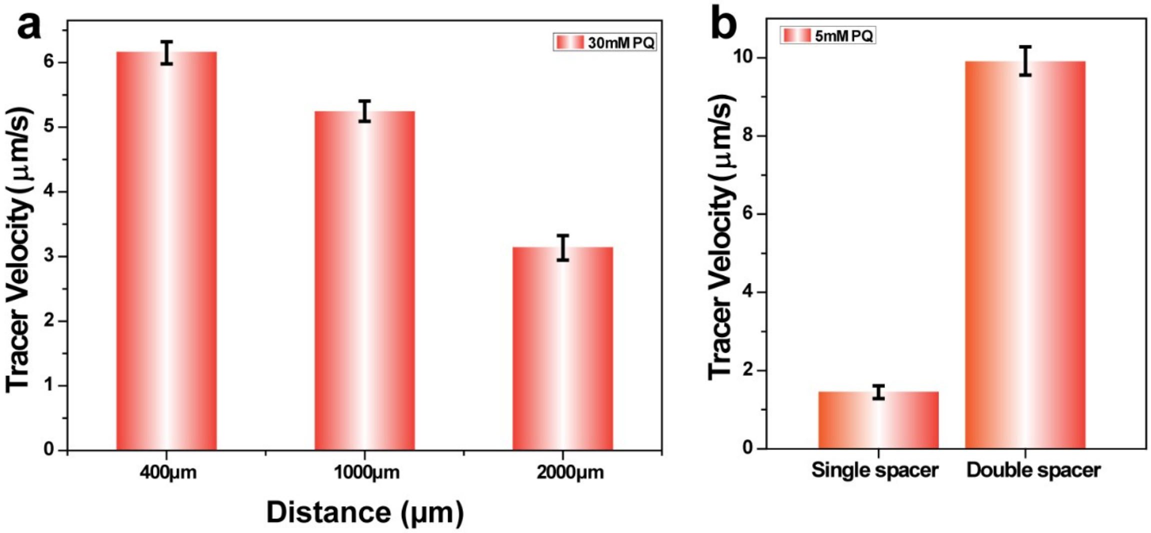


Figure S13. (a)Spatial velocity profile for PQ fuelled micropumps. The experiment was performed in presence of 30 mM PQ (b) The effect of chamber height on fluid velocity. The experiment was performed in presence of 5 mM PQ.

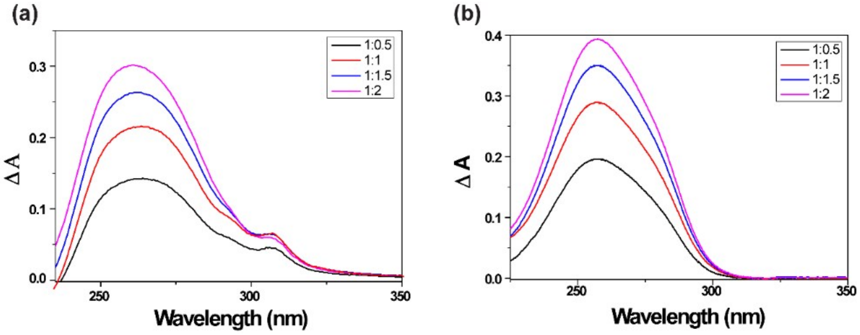
Figure S14. ITC titration of anionic pillar[5]arene (0.050mM) with paraquat (3mM) in water at 298 K.

Isothermal titration calorimetric measurements were performed on a Malvern MicroCal PEAQ-ITC, which is composed of a reference cell and a sample cell of 300 µL. Before each titration, all the solutions were degassed and kept constant temperature. In a typical run, a 40 µL syringe was full of guest (3.00 mM) and the cell was loaded with host (0.050 mM, 300uL). The titration of the host with the guest was carried out at 298 K, with a constant rate of 750 rpm, 30 injections of 1.3 µL, a time interval of 150 s. The enthalpy change per mole of each added paraquat in the sample cell was recorded continuously. The control titrations of paraquat into water were also completed under



the same conditions. The enthalpy changes of the titrations of the blank test were subtracted from the original titration. The Fig 5a and S8 final integration data obtained from the titration were fitted by the “one set of binding sites” model.

11. UV-Vis Titration of Anionic and Cationic Pillar[5]arene with Paraquat



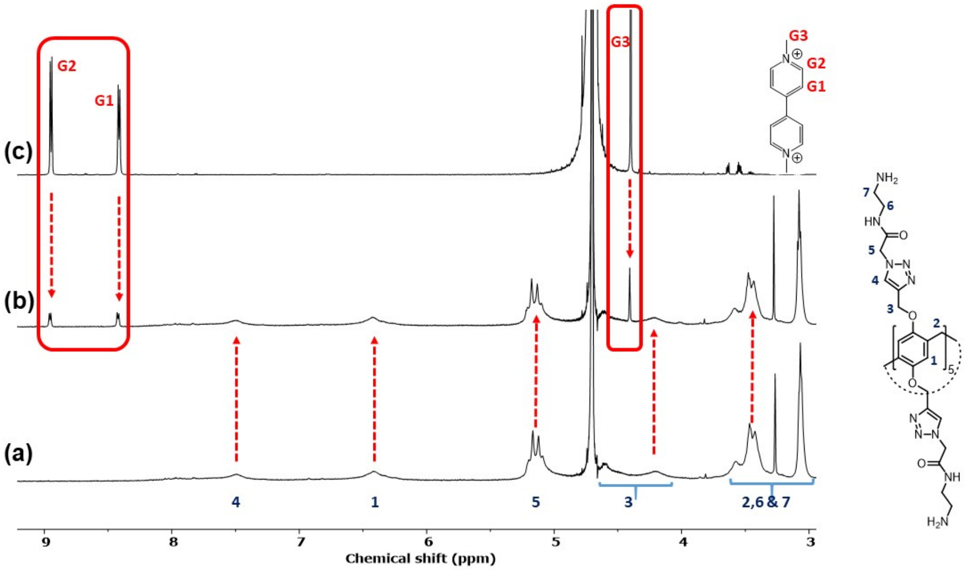


Figure S16. ^{1}H NMR spectra (500 MHz, D_2O): (a) cationic pillar[5]amine (2 mM), (b) cationic pillar[5]arene (2 mM) and guest (2 mM), and (c) guest (2 mM).

12. NMR titration of Cationic Pillar[5]arene with Paraquat

References:

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